Operator representation as a new differential optical absorption spectroscopy formalism

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UV–visible absorption spectroscopy with extraterrestrial light sources is a widely used technique for the measurement of stratospheric and tropospheric trace gases. We focus on differential optical absorption spectroscopy (DOAS) and present an operator notation as a new formalism to describe the different processes in the atmosphere and the simplifying assumptions that compose the advantage of DOAS. This formalism provides tools to classify and reduce possible error sources of DOAS applications. © 2005 Optical Society of America

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1. Introduction

A spectral signal on its way from generation in the light source through the atmosphere to the instrument experiences many different transformations. In this paper we introduce a formalism allowing a comparison of those transformations and the corresponding features of differential optical absorption spectroscopy (DOAS).[1] In this comparison we especially aim at the sequencing of the different transformations, each described by an operator, and identify some combination of noncommuting operators that can be assigned to effects such as the I_0 effect or the undersampling problem. Since these effects are based on different instrument and DOAS parameters, the classification of the main error sources can be helpful for the design of new DOAS instruments and to reduce the errors of existing DOAS applications.

2. Differential Optical Absorption Spectroscopy

In this section we describe the DOAS method. The absorption of radiation by matter is described by the Beer–Lambert law. The absorption of light of the intensity $I(\lambda)$ at the wavelength λ as it passes through an absorbing matter dl is

$$I(\lambda) = I_0(\lambda)\exp\left[-\sigma(\lambda,\ T) \int c(l)\mathrm{d}l \right]. \qquad (1)$$

Here $I_0(\lambda)$ is the incident light intensity, $I(\lambda)$ is the transmitted light intensity, $\sigma(\lambda,\ T)$ is the absorption cross section of the absorbing species that depends on the wavelength and temperature, and $c(l)$ is its concentration. Here the first simplifying assumption is made, namely, the temperature independence of the absorption cross sections. The cross sections can vary with altitude and temperature; therefore excluding it from the integration produces an error. We can reduce this error by using several cross sections for different temperatures, or, if those are linear dependent, by performing *a posteriori* temperature corrections for known temperature profiles. For most applications it is sufficient to use the temperature at the number density maximum of the climatological profile of the corresponding trace gas.[2]

When absorptions are measured in the atmosphere, Eq. (1) has to be applied for the absorption of all trace gases and has to deal with influences of scattering:

$$I(\lambda) = I_0(\lambda)\exp\left[-\sum_i \sigma_i(\lambda)\mathrm{SCD}_i \right]g(\lambda). \qquad (2)$$

where the factor $g(\lambda)$ describes additional attenuation by the optical system and by Rayleigh and Mie scattering in the atmosphere and all other broadband structured influences, such as reflection on the ground. The sum in the exponential runs over all

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